Coordination of Ethene and Propene to a Cationic d0 Vanadium Center

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Supporting Material to:

"Coordination of Ethene and Propene to a Cationic d^0 Vanadium Center"

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Part I: Experimental Section

General

All experiments were performed under nitrogen atmosphere using standard glove-box Schlenk and vacuum line techniques. Deuterated solvents (Aldrich) were either dried over Na/K alloy and vacuum transferred before use (C_6D_6, C_7D_8) or flushed with nitrogen and stored over mol. sieves (C_6D_5Br). Other solvents were distilled from Na or Na/K alloy before use. $B(C_5F_5)_3$[1] and $Cl_3V(N$*t*$-Bu)$[2] were prepared according to literature procedures. $C_5H_5(CH_2)_2NH$*i*-Pr was prepared in analogous fashion to $C_5H_5(CH_2)_3NHMe$[3] from $Br(CH_2)_2NH_2$*i*PrBr and 3 equiv. of CpNa. Ethene and propene (Matheson, C.P.) were used as purchased. NMR spectra were run on Varian Gemini 200, VXR-300 and VXR-500 spectrometers. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

(*t*-BuN)V(NMe_2)$_3$

A solution of $Cl_3V(N$*t*$-Bu)$ (0.73 g, 3.2 mmol) in 50 mL of pentane was cooled to -20°C after which $LiNMe_2$ (0,49 g, 9.6 mmol) was added. The suspension was warmed to room temperature and stirred for one more hour. After filtration, the solvent was removed *in vacuo*. The resulting red oil (0.57 g) consists mainly of (*t*-BuN)V(NMe_2)$_3$ but also contains unknown impurities.(can be up to 15% by NMR). This material is, however, of sufficient purity to use in the subsequent synthesis of (*t*-BuN)V(NMe_2)$_2$Cl.

^{1}H NMR (200 MHz, C_6D_6, 25°C): δ 3.43 (s, 18H, NMe), 1.38 (s, 9H, *t*Bu)

$^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25°C): δ 50.0 (br, NMe), 31.8 (CH_3 of *t*Bu), C_q of *t*Bu not observed

^{51}V NMR (78.9 MHz, C_6D_6, 25°C): δ -267 (t, J_{V-N} = 84 Hz)

IR (neat): 594 (w), 621 (w), 665 (w), 687 (w), 806 (w), 955 (s), 1047 (s), 1119 (s), 1159 (s), 1211 (s), 1236 (s), 1354 (s), 1412 (s), 1445 (s), 2764 (s), 2807 (s), 2845 (s), 2890 (s), 2918 (s), 2967 (s)

Molecular weight (by cryoscopy in benzene). calculated: 254; found: 263

(*t*BuN)VCl(NMe$_2$)$_2$

In 40 mL of pentane 1.56 g (6.1 mmol) of (*t*BuN)V(NMe$_2$)$_3$ and 0.70 g (3.1 mmol) of (*t*BuN)VCl$_3$ were dissolved at ambient temperature and stirred for two hours. The solution was filtered, concentrated to half the volume and cooled to -20°C, yielding 1.82 g (7.4 mmol, 81%) of (*t*BuN)VCl(NMe$_2$)$_2$ as red crystals.

^1H NMR (200 MHz, C_6D_6, 25°C): δ 3.41 (s, 12H, NMe), 1.31 (s, 9H, *t*Bu)

$^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25°C): δ 50.9 (NMe), 30.6 (CH_3 of *t*Bu), C_q of *t*Bu not observed.

^{51}V NMR (78.9 MHz, C_6D_6, 25°C): δ -281 (t, J_{V-N} = 91 Hz)

Anal. Calcd (%) for $C_8H_{21}N_3VCl$, C: 39.11, H: 8.62, N: 17.10, V: 20.74, Cl: 14.43; Found: C: 38.99, H: 8.57, N: 16.79, V: 20.62, Cl: 14.09

Molecular weight (by cryoscopy in benzene). calculated: 246; found: 269

[C$_5$H$_4$(CH$_2$)$_2$N*i*-Pr]V(N*t*-Bu)Cl (1)

To a solution of 3.26 g (13 mmol) of (*t*BuN)VCl(NMe$_2$)$_2$ in 100 mL of pentane 2.00 g (13 mmol) of $C_5H_5CH_2CH_2N(H)iPr$ was added. The brown solution was refluxed for 24 hours, after which the colour had turned to red. All volatile compounds were removed *in vacuo* and the resulting solid was extracted twice with 50 mL of pentane. The pentane solution was concentrated and cooled to -20 °C, yielding 3.31 g (10.8 mmol, 83%) of **1** as a red brown microcrystalline solid. Recrystalization from pentane gives **1** as analytically pure red crystals.

^1H NMR (300 MHz, C_6D_6, 25°C): δ 6.10 (m, 1H, Cp), 5.97 (m, 2H, Cp and *i*Pr), 5.87 (m, 1H, Cp), 5.13 (m, 1H, Cp), 4.66 (m, 1H, NC*H*H), 3.25 (dd, J_{H-H} = 6.3 / 12.6 Hz, 1H, NCH*H*), 2.47 (m, 1H, CpC*H*H), 1.76 (m, 1H,CpCH*H*), 1.19 (s, 9H, *t*Bu), 1.01 (d, J_{H-H} = 7.0 Hz, 3H, *i*Pr), 0.98 (d, J_{H-H} = 7.0 Hz, 3H, *i*Pr)

$^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 25°C): δ 139.6 (C_q of Cp), 115.1, 114.6, 100.5, 99.5 (4 CH of Cp), 72.3 (CH of *i*Pr), 70.5 (NCH_2) , 30.0 ($CpCH_2$), 31.2 (CH_3 of *t*Bu), 21.2, 20.5 (2 CH_3 of *i*Pr), C_q of *t*Bu not observed

^{51}V NMR (78.9 MHz, C_6D_6, 25°C): δ -674 ($\Delta\nu_{½}$ = 365 Hz)

Anal. Calcd (%) for $C_{14}H_{24}N_2VCl$, C: 54.82, H: 7.89, N: 9.13, V: 16.61, Cl: 11.56, found: C: 54.64, H: 7.92, N: 8.96, V: 16.45, Cl: 11.46

Molecular weight (by cryoscopy in benzene). calculated: 307, found: 315

$[C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)Me (2)

1.58 g (5.2 mmol) of **1** was dissolved in 30 mL of pentane and 6.5 mL of 0.88 M MeLi in hexane (5.7 mmol) was added subsequently at ambient temperature. The solution was stirred for an hour, after which all volatile compounds were removed *in vacuo*. The resulting brown solid was extracted twice with 25 mL of pentane and all solvent was removed *in vacuo*, resulting in a brown oil which solidified upon cooling. This yielded 1.09 g (3.8 mmol, 73%) of **3** as a brown powder. Recrystallization from pentane produced red brown crystals of analytically pure **3**, which were also suitable for X-ray diffraction.

^1H NMR (300 MHz, C_6D_6, 25°C): δ 5.83 (m, 1H, Cp), 5.50 (m, 1H, Cp), 5.41 (m, 2H, Cp), 5.29 (sept., J_{H-H} = 6.6 Hz, 1H, *i*Pr), 4.13 (m, 1H, NC*H*H), 3.30 (m, 1H, NCH*H*), 2.50 (ddd, J_{H-H} = 2.5 / 6.6 / 12.8 Hz, 1H, CpC*H*H), 2.07 (m, 1H, CpCH*H*), 1.25 (s, 9H, *t*Bu), 1.15 (d, J_{H-H} = 6.6 Hz, 3H, *i*Pr), 0.95 (d, J_{H-H} = 7.0 Hz, 3H, *i*Pr), 0.69 (br, 3H, VMe).

$^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, -70°C): δ 132.9 (C_q of Cp), 112.7, 107.5, 100.6, 94.1 (4 CH of Cp), 70.4 (C_q of *t*Bu), 67.1 (CH of *i*Pr), 66.5 (NCH_2), 29.4 ($CpCH_2$), 31.2 (CH_3 of *t*Bu), 21.8, 20.7 (2 CH_3 of *i*Pr), 17.7 (br, $\Delta\nu_{½}$ = 300 Hz, VMe)

^{13}C NMR (125.7 MHz, C_6D_6, 25°C): δ 132.27 (s, C_q of Cp), 113.03 (d, 169.6 Hz, Cp CH), 107.92 (d, 172.0 Hz, Cp CH), 100.92 (d, 173.1 Hz, Cp CH), 97.47 (d, 173.2 Hz, Cp CH), 67.48 (d, 142 Hz, *i*-Pr CH), 66.82 (t, 142 Hz, NCH_2), 31.60 (q, 125.8 Hz, CH_3 of *t*Bu), 29.87 (t, 128.6 Hz, $CpCH_2$), 22.17 (q, 124.9 Hz, CH_3 of *i*Pr), 21.07 (q, 124.6 Hz, CH_3 of *i*Pr), 17 (very broad, V-CH_3). *t*Bu C_q not observed.

^{51}V NMR (131.4 MHz, C_6D_6, 25°C): δ -665 ($\Delta\nu_{½}$ = 324 Hz)

Anal. Calcd (%) for $C_{15}H_{27}N_2V$, C: 62.92, H: 9.50, N: 9.78, V: 17.79; found: C: 62.66, H: 9.49, N: 9.80, V: 17.68

$[C_5H_4(CH_2)_2Ni\text{-}Pr]V(Nt\text{-}Bu)[MeB(C_6F_5)_3]$ (3)

43 mg (0.15 mmol) of (*t*BuN)VMe(CpCH_2CH_2N*i*Pr) was dissolved in 2 mL of pentane and slowly added at ambient temperature to a stirred solution of 100 mg (0.19 mmol) of $B(C_6F_5)_3$ in 10 mL of pentane. The resulting orange precipitate was washed three times with 5 mL of pentane and dried *in vacuo*. This yielded 97 mg (0.12 mmol = 81%) of analytically pure **3** as an orange powder.

Anal. Calcd (%) for $C_{33}H_{27}BF_{15}N_2V$, C: 49.65, H: 3.41, N: 3.51, V: 6.38, found: C: 49.78, H: 3.28, N: 3.40, V: 6.31.

3 in C_6D_6:

^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 5.86 (br, 1H, Cp), 5.80 (sept, $J_{H\text{-}H}$ = 6.4 Hz, 1H, *i*Pr), 5.59 (br, 1H, Cp), 5.46 (br, 1H, Cp), 4.74 (m, 1H, NC*H*H), 4.52 (br, 1H, Cp), 2.98 (dd, $J_{H\text{-}H}$ = 7.1 / 13.5 Hz, 1H, NCH*H*), 2.28 (dd, $J_{H\text{-}H}$ = 7.1 / 13.2 Hz, 1H, CpC*H*H), 1.44 (m, 1H, CpCH*H*), 0.84 (s, 9H, *t*Bu), 0.63 (d, $J_{H\text{-}H}$ = 6.3 Hz, 3H, *i*Pr), 0.47 (d, $J_{H\text{-}H}$ = 6.4 Hz, 3H, *i*Pr), -0.20 (br, $\Delta\nu_{½}$ = 23 Hz, 3H, BMe)

$^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 25°C): δ 148.9 (d, $^1J_{C\text{-}F}$ = 242 Hz, C_6F_5), 142.9 (C_q of Cp), 139.3 (d, $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 137.6 (d, $^1J_{C\text{-}F}$ = 245 Hz, C_6F_5), 112.6, 112.3, 102.1, 100.9 (4 CH of Cp), 75.5 (CH of *i*Pr), 72.8 (NCH_2), 29.3 ($CpCH_2$), 30.5 (CH_3 of *t*Bu), 21.3, 20.2 (2 CH_3 of *i*Pr), C_q of *t*Bu and B-Me not observed

^{51}V NMR (131.4 MHz, C_6D_6, 25°C): δ -514 ($\Delta\nu_{½}$ = 1630 Hz)

^{19}F NMR (188.2 MHz, C_6D_6, 25°C): δ -134.9 (ortho), -162.2 (para), -166.8 (meta), Δδ (*p-m*) = 4.6 ppm.

3 in C_6D_5Br:

^{1}H NMR (200 MHz, C_6D_5Br, 25°C): δ 6.06 (br, 1H, Cp), 5.73 (sept, $J_{H\text{-}H}$ = 6.4 Hz, 1H, *i*Pr), 5.52 (br, 1H, Cp), 5.37 (br, 1H, Cp), 5.13 (br, 1H, Cp), 4.70 (m, 1H, NC*H*H), 3.56 (dd, $J_{H\text{-}H}$ = 6.6 / 12.9 Hz, 1H, NCH*H*), 2.70 (dd, $J_{H\text{-}H}$ = 6.5 / 13.2 Hz, 1H, CpC*H*H), 2.09 (m, 1H, CpCH*H*), 1.13 (br, 3H, BMe), 1.01 (s, 9H, *t*Bu), 0.99 (shoulder, *i*Pr), 0.76 (d, $J_{H\text{-}H}$ = 6.3 Hz, 3H, *i*Pr)

$^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_5Br, 25°C): δ 148.9 (d, $^1J_{C\text{-}F}$ = 239 Hz, C_6F_5), 143.2 (C_q of Cp), 138.0 (d, $^1J_{C\text{-}F}$ = 241 Hz, C_6F_5), 136.0 (d, $^1J_{C\text{-}F}$ = 248 Hz, C_6F_5), 112.8, 110.8, 103.4, 103.0 (4 CH of Cp), 75.8 (CH of *i*Pr), 73.9, 29.2 (CH_2CH_2), 30.7 (CH_3 of *t*Bu), 22.3, 20.7 (2 CH_3 of *i*Pr), 11.5 (br, $\Delta\nu_{½}$ ~ 100 Hz, B-Me), C_q of *t*Bu not observed

^{51}V NMR (131.4 MHz, C_6D_5Br, 25°C): δ -544 ($\Delta\nu_{½}$ = 1276 Hz)

^{19}F NMR (188.2 MHz, C_6D_5Br, 25°C): δ -133.4 (ortho), -165.7 (para), -168.1 (meta), Δδ (*p-m*) = 2.4 ppm.

[$C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)(THF)[$MeB(C_6F_5)_3$]

A solution of **2** (20 mg, 0.07 mmol) in 0.1 mL of C_6D_5Br was added to a solution of $B(C_6F_5)_3$ (10 mg, 0.08 mmol) in 0.4 mL of C_6D_5Br. THF (6 μl, 0.07 mmol) was added subsequently by microsyringe. Addition of several equivalents of THF did not lead to observable broadening of the resonances of free or coordinated THF at ambient temperature.

^{1}H NMR (500 MHz, C_6D_5Br, 25°C): δ 6.12 (m, 1H, Cp), 5.89 (m, 1H, Cp), 5.64 (sept, J_{H-H} = 6.6 Hz, 1H, *i*Pr), 5.37 (m, 1H, Cp), 5.02 (m, 1H, Cp), 4.93 (m, 1H, NC*H*H), 3.48 (m, 1H, NCH*H*), 3.42 (m, 2H, α-H THF), 3.32 (m, 2H, α-H THF), 2.75 (m, 1H, CpC*H*H), 2.01 (m, 1H, CpCH*H*), 1.52 (m, 4H, β-H THF), 1.08 (br, 3H, BMe), 1.02 (s, 9H, *t*Bu), 0.93 (d, J_{H-H} = 6.6 Hz, 3H, *i*Pr), 0.73 (d, J_{H-H} = 6.6 Hz, 3H, *i*Pr)

^{13}C{^{1}H} NMR (125.7 MHz, C_6D_5Br, 25°C): δ 149.4 (d, $^1J_{C-F}$ = 255 Hz, C_6F_5), 143.2 (C_q of Cp), 138.3 (d, $^1J_{C-F}$ = 250 Hz, C_6F_5), 137.3 (d, $^1J_{C-F}$ = 255 Hz, C_6F_5), 112.4, 111.8 (2 CH of Cp), 102.7 (br, 2 CH of Cp), 80.8 (α-C THF), 75.0 (CH of *i*Pr), 73.2 (NCH_2), 30.1 ($CpCH_2$), 31.6 (CH_3 of *t*Bu), 26.5 (β-C THF), 22.2, 22.0 (2 CH_3 of *i*Pr), 11.7 (br, $\Delta\nu_{½}$ = 100 Hz, B-Me), C_q of *t*Bu not observed

^{51}V NMR (131.4 MHz, C_6D_5Br, 25°C): δ -567 ($\Delta\nu_{½}$ = 936 Hz)

^{19}F NMR (188.2 MHz, C_6D_5Br, 25°C): δ -133.3 (ortho), -165.4 (para), -168.0 (meta), Δδ (*p-m*) = 2.6 ppm

[$C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)(PMe_3)[$MeB(C_6F_5)_3$]

A solution of **2** (20 mg, 0.07 mmol) in 0.1 mL of C_6D_5Br was added to a solution of $B(C_6F_5)_3$ (10 mg, 0.08 mmol) in 0.4 mL of C_6D_5Br. PMe_3 (7 μl, 0.07 mmol) was added subsequently by microsyringe

^{1}H NMR (500 MHz, C_6D_5Br, 25°C): δ 5.58 (br, 1H, Cp), 5.52 (br, 1H, Cp), 5.50 (br, 1H, Cp), 5.33 (sept, J_{H-H} = 6.6 HZ, 1H, *i*Pr), 5.01 (br, 1H, Cp), 4.11 (m, 1H, NC*H*H), 3.36 (m, 1H, NCH*H*), 2.42 (m, 1H, CpC*H*H), 2.09 (m, 1H, CpCH*H*), 1.14 (br, 3H, BMe), 0.98 (d, J_{P-H} = 9.8 Hz, 9H, PMe_3), 0.91 (s, 9H, *t*Bu), 0.93 (d, J_{H-H} = 6.8 Hz, 3H, *i*Pr), 0.62 (d, J_{H-H} = 6.8 Hz, 3H, *i*Pr)

$^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_5Br, 25°C): δ 149.4 (d, $^1J_{C-F}$ = 244, C_6F_5), 138.2 (d, $^1J_{C-F}$ = 246, C_6F_5), 137.3 (d, $^1J_{C-F}$ = 244, C_6F_5), 137.2 (C_q of Cp), 108.6, 106.2, 104.7, 100.3 (4 CH of Cp), 73.1 (CH of *i*Pr), 70.7(NCH_2), 29.1 ($CpCH_2$), 31.8 (CH_3 of *t*Bu), 23.5, 21.4 (2 CH_3 of *i*Pr), 17.3 (d, J_{P-C} = 28 Hz). BMe and C_q of *t*Bu not observed.

^{51}V NMR (131.4 MHz, C_6D_5Br, 25°C): δ -832 (d, J_{P-V} = 280 Hz)

^{19}F NMR (188.2 MHz, C_6D_5Br, 25°C): δ -133.3 (ortho), -165.3 (para), -167.9 (meta), Δδ (*p-m*) = 2.6 ppm.

^{31}P NMR (202 MHz, C_6D_5Br, 25°C): δ 7 (plateau, $\Delta\nu_{top}$ = 2225 Hz)

$[C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)(η-C_2H_4)[MeB(C_6F_5)$_3$] (4a)

A solution of **2** (20 mg, 0.07 mmol) in 0.1 mL of C_6D_5Br was added to a solution of $B(C_6F_5)_3$ (10 mg, 0.08 mmol) in 0.4 mL of C_6D_5Br. This solution was transferred into an NMR tube equipped with a Teflon (Young) valve. The tube was connected to a high vacuum line, frozen and evacuated. Subsequently 0.25 mmol of ethene was condensed into the tube, which was then closed and thawed out.

^1H NMR (500 MHz, C_6D_5Br, -30°C): δ 5.71 (br, 1H, Cp), 5.61 (br, 1H, Cp), 5.34 (sept, J_{H-H} = 6.4 Hz, 1H, *i*Pr), 5.27 (br, 1H, Cp), 5.02 (br, 1H, Cp), 4.72 (m, 2H, =C*H*H), 4.61 (m, 1H, NC*H*H), 4.33 (m, 2H, =CH*H*), 3.26 (dd, J_{H-H} = 7.3 / 14.6 Hz, 1H, NCH*H*), 2.70 (dd, J_{H-H} = 6.8 / 13.3 Hz, 1H, CpC*H*H), 1.91 (m, 1H, CpCH*H*), 1.19 (br, 3H, BMe), 0.94 (s, 9H, *t*Bu), 0.82 (d, J_{H-H} = 6.4 Hz, 3H, *i*Pr), 0.59 (d, J_{H-H} = 6.7 Hz, 3H, *i*Pr).

^{13}C NMR (125.7 MHz, C_6D_5Br, -30°C): δ 149.3 (d, $^1J_{C-F}$ = 241 Hz, C_6F_5), 141.9 (C_q of Cp), 138.3 (d, $^1J_{C-F}$ = 244 Hz, C_6F_5), 137.3 (d, $^1J_{C-F}$ = 248 Hz, C_6F_5), 109.6, 109.2, 103.1, 101.3 (d, 173.4, 173.5, 179.1 and 181.0 Hz respectively, 4 CH of Cp), 103.2 (=CH_2, d, 164 Hz), 76.3 (d, 141.7 Hz, CH of *i*Pr), 73.3 (t, 138.0 Hz, NCH_2), 29.5 (t, partial overlap, $CpCH_2$), 31.1 (q, 131.8 Hz, CH_3 of *t*Bu), 22.6, 20.7 (q, 126.8 Hz, 2 CH_3 of *i*Pr), 11.8 (br, $\Delta\nu_{½}$ = 75 Hz, B-Me), C_q of *t*Bu not observed

^{51}V NMR (131.4 MHz, C_6D_5Br, -30°C): δ -707 ($\Delta\nu_{½}$ = 751 Hz)

^{19}F NMR (188.2 MHz, C_6D_5Br, 25°C): δ -133.2 (ortho), -165.3 (para), -167.9 (meta), Δδ (*p-m*) = 2.6 ppm.

[$C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)(η-C_2H_3Me)[$MeB(C_6F_5)_3$] (4b)

The same procedure was followed as described for the ethene adduct **4a**, now using propene. Two isomers are formed (A, B) in approximately equal amounts (A : B ≈ 5 : 4). The assignment of the propene ^{1}H-resonances for the two isomers was aided by 2D ^{1}H,^{1}H-COSY NMR.

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): δ 6.26^B, 6.01^A (m, =C*H*Me), 5.98, 5.93, 5.55, 5.43, 5.40, 5.34, 5.30, 5.08 (m, Cp), 5.66, 5.42 (*i*Pr CH), 4.65, 4.39 (m, NC*H*H), 4.33^B, 4.01^A (d, J_{H-H} = 16.6^B, 17.1^A Hz, =C*H*H cis to Me), 4.15^A, 3.65^B (d, J_{H-H} = 8.8^A, 8.3^B Hz, =CH*H* trans to Me), 3.31, 3.16 (m, NCH*H*), 2.58, 2.54 (m, CpC*H*H), 1.99, 1.88 (m, CpCH*H*), 1.32^A, 1.28^B (d, J_{H-H} = 5.1^A, 5.5^B Hz, =CH*Me*), 1.19 (br, BMe), 0.98, 0.95 (s, *t*Bu), 0.80, 0.72, 0.66, 0.56 (d, J_{H-H} = 5.7 Hz, *i*Pr Me).

^{13}C NMR (125.7 MHz, C_6D_5Br, -30°C): d 149.4 (d, $^1J_{C-F}$ = 235 Hz, C_6F_5), 142.2, 141.8 (s, C_q of Cp), 138.3 (d, $^1J_{C-F}$ = 243 Hz, C_6F_5), 137.7, 135.4 (d, J_{C-H} = 156.6, 158.8 Hz, =C*H*Me), 137.3 (d, $^1J_{C-F}$ = 244 Hz, C_6F_5), 111.2, 110.3, 109.6, 109.2 (d, J_{C-H} = 181.8, 176.5, 174.8, 172.9 Hz, CH of Cp), 102.4, 102.3 (d, J_{C-H} = 174 Hz, CH of Cp), 101.3, 101.2 (d, J_{C-H} = 177 Hz, CH of Cp), 92.7, 92.5 (t, J_{C-H} = 160.2, 158.6 Hz, =CH_2), 77.0, 76.4 (t, NCH_2), 73.4, 72.7 (d, CH of *i*Pr), 31.2, 30.9 (q, J_{C-H} = 127.4, 128.2, CH_3 of *t*Bu), 29.7, 29.5 (m, CpCH_2), 23.4, 22.9, 22.8, 22.6 (m, 2 CH_3 of *i*Pr), 20.2, 20.1 (m, =CH*Me*). C_q of *t*Bu not observed.

^{51}V NMR (131.4 MHz, C_6D_5Br, -30°C): δ -646, -650

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Supporting Material to:

"Coordination of Ethene and Propene to a Cationic d^0 Vanadium Center"

by P.T. Witte, A. Meetsma, B. Hessen and P.H.M. Budzelaar

Part II: Quantumchemical Calculations

Details of DFT/B3LYP calculations:

Basis sets used: 3-21G on C,N,H (Binkley, J.S.; Pople, J.A.; Hehre, W.J. *J. Am. Chem. Soc.* **1980**, *102*, 939), LanL2DZ ECP on V (Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 270). All geometries were fully optimized, without any symmetry restrictions.

Obtained Z-matrices and geometrical parameters for the various species are given below.

$[C_5H_4(CH_2)_2NH]V(NH)^+$:

Total energy: -451.31247 a.u.

```
v
x 1 vx1
c 2 cx1 1 90
c 2 cx2 3 72 1 tc2
c 2 cx3 3 cxc3 4 180
c 2 cx4 4 cxc4 3 tc4
c 2 cx5 5 cxc5 3 tc5
c 3 cc6 4 ccc6 5 tc6
h 4 ch7 3 cch7 5 th7
h 5 ch8 3 cch8 4 th8
h 6 ch9 4 cch9 3 th9
h 7 ch10 5 cch10 3 th10
c 8 cc11 3 ccc11 1 tc11
h 8 ch12 3 cch12 13 th12
h 8 ch13 3 cch13 13 th13
n 13 cn 8 ccn 1 tn
h 13 ch14 8 cch14 16 th14
h 13 ch15 8 cch15 16 th15
h 16 nh 13 cnh 1 tnh
```

```
n 1 vn 2 xvn 16 tvn
x 20 1 1 90 2 0
h 20 nhi 21 xnhi 1 thi

vn                      1.6390736111
xvn                   131.0486257757
tvn                   134.6616976318
nhi                     1.0294772955
xnhi                   83.3676510227
thi                   181.5749089393
vx1                     1.9627184165
cx1                     1.2846465650
cx2                     1.1761017277
cx3                     1.2906738939
cx4                     1.1477642860
cx5                     1.2079317392
tc2                    88.3821776457
cxc3                   66.9197515979
cxc4                   76.3214160582
cxc5                   70.4268262619
tc4                   183.2846150000
tc5                   178.7427785580
cc6                     1.5062871640
ch7                     1.0798867203
ch8                     1.0812519976
ch9                     1.0784579417
ch10                    1.0805905260
ccc6                  124.1811536433
cch7                  125.4055644515
cch8                  126.0541526756
cch9                  126.2191645205
cch10                 125.8868489994
tc6                   195.4032453248
th7                   181.2517607429
th8                   181.8648255837
th9                   182.2114650497
th10                  179.0286844978
cc11                    1.5587709635
ccc11                 108.2895962375
tc11                   19.9366394394
ch12                    1.0944338028
ch13                    1.0934283661
ch14                    1.0961642124
ch15                    1.0938675832
cch12                 111.4231024191
cch13                 109.3518599897
cch14                 110.3568279624
cch15                 111.6580151151
th12                  120.8293505418
th13                 -119.3637245018
th14                  117.9622697349
th15                 -121.3633472068
cn                      1.5070915134
ccn                   108.3228277896
tn                    -16.3367456126
nh                      1.0288581581
cnh                   113.0480107261
tnh                   184.1486353550
```

$[C_5H_4(CH_2)_2NH]V(NH)(C_2H_4)^+$ (lowest-energy conformation, olefin parallel to V-imido) :

Total energy: -529.52307 a.u.

```
v
x 1 vx1
c 2 cx1 1 90
c 2 cx2 3 72 1 tc2
c 2 cx3 3 cxc3 4 180
c 2 cx4 4 cxc4 3 tc4
c 2 cx5 5 cxc5 3 tc5
c 3 cc6 4 ccc6 5 tc6
h 4 ch7 3 cch7 5 th7
h 5 ch8 3 cch8 4 th8
h 6 ch9 4 cch9 3 th9
```

```
h 7 ch10 5 cch10 3 th10
c 8 cc11 3 ccc11 1 tc11
h 8 ch12 3 cch12 13 th12
h 8 ch13 3 cch13 13 th13
n 13 cn 8 ccn 1 tn
h 13 ch14 8 cch14 16 th14
h 13 ch15 8 cch15 16 th15
h 16 nh 13 cnh 1 tnh
n 1 vn 2 xvn 16 tvn
x 20 1 1 90 2 0
h 20 nhi 21 xnhi 1 thi
x 1 vx2 2 xvx 16 tvx
c 23 cx 1 vxc 2 tx
x 23 1 24 90 1 0
c 23 cx 25 90 24 180
h 24 che1 26 cche1 1 te1
h 24 che2 26 cche2 27 te2
h 26 che3 24 cche3 27 te3
h 26 che4 24 cche4 29 te4

vn                      1.6441219620
xvn                   127.5816581574
tvn                   125.5671385497
nhi                     1.0294561284
xnhi                   81.7032086279
thi                   183.2611237304
vx2                     2.3886849349
xvx                   121.1112457770
cx                      0.6818237182
vxc                    85.1489768078
tx                     39.5409633576
che1                    1.0861998048
che2                    1.0839084674
che3                    1.0843106421
che4                    1.0849139041
cche1                 120.6803815150
cche2                 120.5698006606
cche3                 121.2670902972
cche4                 121.1822925436
te1                    93.0116766304
te2                   165.4283853147
te3                     2.9524515183
te4                  -172.0265672835
tvx                  -117.1074167046
vx1                     1.9876426650
cx1                     1.2578278620
cx2                     1.1951203580
cx3                     1.2535838605
cx4                     1.1791974146
cx5                     1.2032749794
tc2                    86.7853442707
cxc3                   68.8643703546
cxc4                   74.2484547554
cxc5                   71.6414967876
tc4                   183.0439727260
tc5                   178.3239464097
cc6                     1.5054140215
ch7                     1.0793152088
ch8                     1.0802783114
ch9                     1.0783944404
ch10                    1.0794580867
ccc6                  124.3748133780
cch7                  125.4147317762
cch8                  126.0174833767
cch9                  126.1486907117
cch10                 126.0088890097
tc6                   194.4103094658
th7                   180.5699409667
th8                   180.9876271993
th9                   182.1639095527
th10                  178.2809745751
cc11                    1.5582100356
ccc11                 107.7028874553
tc11                   20.3268236979
ch12                    1.0945502218
ch13                    1.0935871192
ch14                    1.0955662421
ch15                    1.0939469598
cch12                 111.5674877835
cch13                 109.4979642275
```

```
cch14                109.8291338330
cch15                111.8276106225
th12                 120.6757978527
th13                -119.2210580108
th14                 117.9508105790
th15                -121.4882520062
cn                     1.5045197119
ccn                  107.7046063287
tn                   -18.9402658336
nh                     1.0268102422
cnh                  113.5619538683
tnh                  188.3335190907
```

$[C_5H_4(CH_2)_2NH]V(NH)(C_2H_4)^+$ (less stable conformation, olefin parallel to V-amido) :

Total energy: -529.52131 a.u.

```
v
x 1 vx1
c 2 cx1 1 90
c 2 cx2 3 72 1 tc2
c 2 cx3 3 cxc3 4 180
c 2 cx4 4 cxc4 3 tc4
c 2 cx5 5 cxc5 3 tc5
c 3 cc6 4 ccc6 5 tc6
h 4 ch7 3 cch7 5 th7
h 5 ch8 3 cch8 4 th8
h 6 ch9 4 cch9 3 th9
h 7 ch10 5 cch10 3 th10
c 8 cc11 3 ccc11 1 tc11
h 8 ch12 3 cch12 13 th12
h 8 ch13 3 cch13 13 th13
n 13 cn 8 ccn 1 tn
h 13 ch14 8 cch14 16 th14
h 13 ch15 8 cch15 16 th15
h 16 nh 13 cnh 1 tnh
n 1 vn 2 xvn 16 tvn
x 20 1 1 90 2 0
h 20 nhi 21 xnhi 1 thi
x 1 vx2 2 xvx 16 tvx
c 23 cx 1 vxc 2 tx
x 23 1 24 90 1 0
c 23 cx 25 90 24 180
h 24 che1 26 cche1 1 te1
h 24 che2 26 cche2 27 te2
h 26 che3 24 cche3 27 te3
h 26 che4 24 cche4 29 te4

vn                     1.6384174313
xvn                  126.7863927377
tvn                  125.2651897917
nhi                    1.0294508367
xnhi                  79.4010642070
thi                  180.3682598228
vx2                    2.4271402456
xvx                  118.6223171149
cx                     0.6792254580
vxc                   88.2458136905
tx                   -47.3962147288
che1                   1.0839349262
che2                   1.0867342739
che3                   1.0849932807
che4                   1.0850620738
cche1                120.8998243506
cche2                120.9708711172
cche3                121.2298480406
cche4                121.2103674755
te1                  102.4992847599
te2                  168.7566971467
te3                    2.6018013477
te4                 -172.9771042656
tvx                 -108.6041500670
vx1                    1.9889656081
cx1                    1.2735655934
cx2                    1.1828064034
cx3                    1.2753330454
```

cx4	1.1576969430
cx5	1.2032961465
tc2	87.1537561329
cxc3	67.5053144645
cxc4	75.3995269658
cxc5	71.0192646221
tc4	182.9500076476
tc5	178.7462163048
cc6	1.5055092734
ch7	1.0793787101
ch8	1.0807228203
ch9	1.0782621461
ch10	1.0788918670
ccc6	123.9365006647
cch7	125.3797813507
cch8	126.0214940812
cch9	126.2277588875
cch10	126.0461312664
tc6	194.5701646907
th7	180.8970998677
th8	181.5348018937
th9	182.2922520988
th10	177.6186353639
cc11	1.5608030042
ccc11	108.1348976328
tc11	18.1707835148
ch12	1.0942909250
ch13	1.0935553686
ch14	1.0959684169
ch15	1.0939840022
cch12	111.5474342606
cch13	109.4624408442
cch14	109.7185529786
cch15	111.8069841418
th12	120.6952784177
th13	-119.3264822451
th14	118.0619643913
th15	-121.6177404679
cn	1.5034983999
ccn	108.0959365028
tn	-18.6755593323
nh	1.0274082125
cnh	113.5052310466
tnh	185.8944377568

Ethene :

Total energy: -78.16105 a.u.

Supporting Material to:

"Coordination of Ethene and Propene to a Cationic d^0 Vanadium Center"

by P.T. Witte, A. Meetsma, B. Hessen and P.H.M. Budzelaar

Part III: Crystal Structure Determination

of **$[C_5H_4(CH_2)_2N$*i*-Pr]V(N*t*-Bu)Me (2)**

Abstract. "IUPAC-name", $C_{15}H_{27}N_2V$, M = 286.33, orthorhombic, *Pbca*, a = 9.556(1), b = 11.492(1), c = 28.941(4) Å, V = 3181.6(6) Å, Z = 8, D_x = 1.195 g cm^{-3}, λ(MoKα) = 0.71073 Å, μ = 6.11 cm^{-1}, F(000) = 1232, T = 130 K, $wR(F^2)$ = 0.1031 for 3148 reflections with $F_o^2 \geq 0$ and 271 parameters and $R(F)$ = 0.0467 for 2246 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

The asymmetric unit consists of one molecule of the title compound.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Suitable red colored block-shaped crystals were obtained by recrystallisation from ....

The crystal, a parallelepiped of approximate size 0.25 x 0.25 x 0.30 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*[2] diffractometer (Mo tube, 50 kV, 40 mA, monochromated Mo-Kα radiation, $\Delta\omega = 0.80 + 0.34$ tg θ), interfaced to a *MSDOS* computer.

Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 22 reflections in the range 15.92° < θ < 20.69°.The unit cell was identified as orthorhombic, space group *Pbca*. Reduced cell calculations did not indicate any higher metric lattice symmetry[5] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. A 360° ψ-scan for a reflection close to axial (-106) showed a variation in intensity of 6% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined.

Final refinement converged at $wR(F^2)$ = 0.1031 for 3148 reflections with $F_o^2 \geq 0$ and 271 parameters and $R(F)$ = 0.0467 for 2246 reflections with $F_o \geq 4.0\ \sigma(F_o)$. A final difference Fourier map did not show residual peaks outside the range ±0.34(7) e/Å^{-3}. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \Sigma_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_o and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates equivalent displacement for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Tables of hydrogen atom positions, thermal displacement parameters, comprehensive distances and angles and tables of (F_o), (F_c) and $\sigma(F_o)$ are given as supplementary material[*3] for this paper. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography.*[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

Results and discussion.

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 1.; the packing of the molecules is shown in the unit cell in Fig. 2. Each asymmetric unit contains one formula unit molecule with no atom setting at special position. The orthorhombic unit cell contains eight discrete molecules (residues) (Fig. 2) of the title compound separated by normal van der Waals distances.[17]

No missed symmetry or solvent-accessible voids were detected by procedures implemented in *PLATON.*[16,17]

[*3] Supplementary Material Available: Tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (.. pages) and an *ORTEP*[14] plot; a listing of observed and calculated structure factors (.. pages). Ordering information is given on any current masthead page.

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Legends to the Figures.

Fig. 1 *PLUTO* drawing of the molecule illustrating the puckering and the adopted numbering scheme.

Fig. 2. Projections of the crystal structure down the axes and one projection with minimal overlap.

Fig. 3. Perspective *ORTEP*[14] drawing the title compound with the atom labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius.

Table 1.

a. Crystal data and details of the structure determination.

Chemical formula	$C_{15}H_{27}N_2V$
Formula weight, g.mol^{-1}	286.33
Crystal system	orthorhombic
Space group, no.[18]	*Pbca,* 61
a, Å	9.566(1)
b, Å	11.492(1)
c, Å	28.941(4)
V, Å	3181.6(6)
Z	8
D_{calc}, g.cm^{-3}	1.195
F(000), electrons	1232
μ(Mo K$\bar{\alpha}$), cm^{-1}	6.11
Approx. crystal dimension, mm	0.25 x 0.25 x 0.30

b. Data collection.

Radiation	Mo $K\bar{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.41, 27.5
ω/2θ scan, deg	$\Delta\omega = 0.80 + 0.34 \text{ tg } \theta$
Data set	h: -12→3; k: 0→14; l: 0→37
Crystal-to-receiving-aperturedistance, mm	173
Horizontal, vertical	
aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	202, 1.0
r.m.s. dev. in %	122, 0.9
	-1-14, 1.0
Drift correction	1.000 - 1.007
X-ray exposure time, h	79.6
Total data	5267
Unique data	3641
Data with criterion: ($F_o \geq 4.0\ \sigma(F_o)$)	2246
$R_{int} = \Sigma [\lvert F_o^2 - F_o^2 (\text{mean})\rvert] / \Sigma [F_o^2]$	0.052
$R_{sig} = \Sigma \sigma(F_o^2) / \Sigma [F_o^2]$	0.044

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	3148
Number of refined parameters	271
Final agreement factors:	
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	0.103
for $F_o^2 > 0$	
Weighting scheme: *a, b*	0.0506, 0.0
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.0467
for $F_o > 4.0\ \sigma(F_o)$	
GooF = S =	
$= [\Sigma w [(\|F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.032
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-0.28, 0.34(7)
Max. (shift/σ) final cycle	< 0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses. Atoms of the Asymmetric Unit.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
V(1)	0.07729(4)	0.20183(4)	0.15305(1)	0.0182(1)
N(1)	-0.0790(2)	0.10922(19)	0.14405(7)	0.0215(7)
N(2)	0.1210(2)	0.2509(2)	0.10123(8)	0.0213(6)
C(1)	0.2308(3)	0.0641(3)	0.17653(11)	0.0309(10)
C(2)	0.2963(3)	0.1722(3)	0.18370(11)	0.0307(10)
C(3)	0.2213(3)	0.2321(3)	0.21750(11)	0.0318(10)
C(4)	0.1104(3)	0.1601(3)	0.23198(10)	0.0291(9)
C(5)	0.1152(3)	0.0559(3)	0.20670(11)	0.0303(9)
C(6)	-0.0001(4)	-0.0310(3)	0.20155(14)	0.0413(12)
C(7)	-0.1263(3)	0.0289(3)	0.18061(12)	0.0326(10)
C(8)	-0.1754(3)	0.1176(3)	0.10422(11)	0.0262(9)
C(9)	-0.1781(4)	0.0056(3)	0.07594(13)	0.0371(11)
C(10)	-0.3217(4)	0.1535(4)	0.11957(16)	0.0396(13)
C(11)	0.1698(3)	0.2949(3)	0.05742(9)	0.0243(8)
C(12)	0.3195(4)	0.3387(4)	0.06240(15)	0.0449(13)
C(13)	0.1647(5)	0.1994(4)	0.02163(13)	0.0499(15)
C(14)	0.0754(5)	0.3954(4)	0.04390(17)	0.0560(16)
C(15)	-0.0325(3)	0.3507(3)	0.17476(12)	0.0272(9)

*) $U_{eq} = 1/3\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$

Table 3. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

V(1)	-N(1)	1.854(2)	C(1)	-C(5)	1.412(4)
V(1)	-N(2)	1.656(2)	C(2)	-C(3)	1.395(4)
V(1)	-C(1)	2.263(3)	C(3)	-C(4)	1.409(4)
V(1)	-C(2)	2.300(3)	C(4)	-C(5)	1.404(5)
V(1)	-C(3)	2.345(3)	C(5)	-C(6)	1.495(5)
V(1)	-C(4)	2.356(3)	C(6)	-C(7)	1.516(5)
V(1)	-C(5)	2.314(3)	C(8)	-C(9)	1.526(5)
V(1)	-C(15)	2.103(3)	C(8)	-C(10)	1.525(5)
N(1)	-C(7)	1.475(4)	C(11)	-C(12)	1.525(5)
N(1)	-C(8)	1.479(4)	C(11)	-C(13)	1.510(5)
N(2)	-C(11)	1.443(4)	C(11)	-C(14)	1.517(6)
C(1)	-C(2)	1.407(5)			

Bond angles (deg.)

N(1)	-V(1)	-N(2)	105.78(10)	V(1)	-N(2)	-C(11)	175.61(18)
N(1)	-V(1)	-C(1)	99.44(10)	V(1)	-C(1)	-C(2)	73.48(19)
N(1)	-V(1)	-C(2)	134.73(11)	V(1)	-C(1)	-C(5)	73.99(18)
N(1)	-V(1)	-C(3)	132.13(10)	C(2)	-C(1)	-C(5)	108.5(3)
N(1)	-V(1)	-C(4)	97.34(10)	V(1)	-C(2)	-C(1)	70.62(17)
N(1)	-V(1)	-C(5)	78.73(10)	V(1)	-C(2)	-C(3)	74.27(17)
N(1)	-V(1)	-C(15)	96.10(11)	C(1)	-C(2)	-C(3)	108.1(3)
N(2)	-V(1)	-C(1)	110.26(11)	V(1)	-C(3)	-C(2)	70.80(18)
N(2)	-V(1)	-C(2)	99.77(11)	V(1)	-C(3)	-C(4)	72.97(17)
N(2)	-V(1)	-C(3)	121.44(11)	C(2)	-C(3)	-C(4)	107.8(3)
N(2)	-V(1)	-C(4)	156.02(10)	V(1)	-C(4)	-C(3)	72.14(18)
N(2)	-V(1)	-C(5)	144.58(11)	V(1)	-C(4)	-C(5)	70.89(18)
N(2)	-V(1)	-C(15)	96.87(12)	C(3)	-C(4)	-C(5)	108.7(3)
C(1)	-V(1)	-C(2)	35.89(12)	V(1)	-C(5)	-C(1)	70.09(19)
C(1)	-V(1)	-C(3)	58.92(12)	V(1)	-C(5)	-C(4)	74.12(19)
C(1)	-V(1)	-C(4)	58.62(11)	V(1)	-C(5)	-C(6)	107.5(2)
C(1)	-V(1)	-C(5)	35.92(11)	C(1)	-C(5)	-C(4)	106.9(3)
C(1)	-V(1)	-C(15)	143.42(12)	C(1)	-C(5)	-C(6)	124.1(3)
C(2)	-V(1)	-C(3)	34.93(11)	C(4)	-C(5)	-C(6)	126.7(3)
C(2)	-V(1)	-C(4)	58.23(11)	C(5)	-C(6)	-C(7)	108.9(3)
C(2)	-V(1)	-C(5)	59.42(11)	N(1)	-C(7)	-C(6)	109.1(2)
C(2)	-V(1)	-C(15)	117.38(12)	N(1)	-C(8)	-C(9)	111.9(3)
C(3)	-V(1)	-C(4)	34.89(11)	N(1)	-C(8)	-C(10)	111.3(3)
C(3)	-V(1)	-C(5)	58.78(11)	C(9)	-C(8)	-C(10)	111.7(3)
C(3)	-V(1)	-C(15)	86.28(12)	N(2)	-C(11)	-C(12)	109.7(2)
C(4)	-V(1)	-C(5)	34.98(12)	N(2)	-C(11)	-C(13)	109.7(3)
C(4)	-V(1)	-C(15)	86.74(12)	N(2)	-C(11)	-C(14)	107.5(3)
C(5)	-V(1)	-C(15)	117.86(12)	C(12)	-C(11)	-C(13)	109.6(3)
V(1)	-N(1)	-C(7)	120.39(17)	C(12)	-C(11)	-C(14)	109.4(3)
V(1)	-N(1)	-C(8)	125.09(18)	C(13)	-C(11)	-C(14)	110.9(3)
C(7)	-N(1)	-C(8)	114.1(2)				

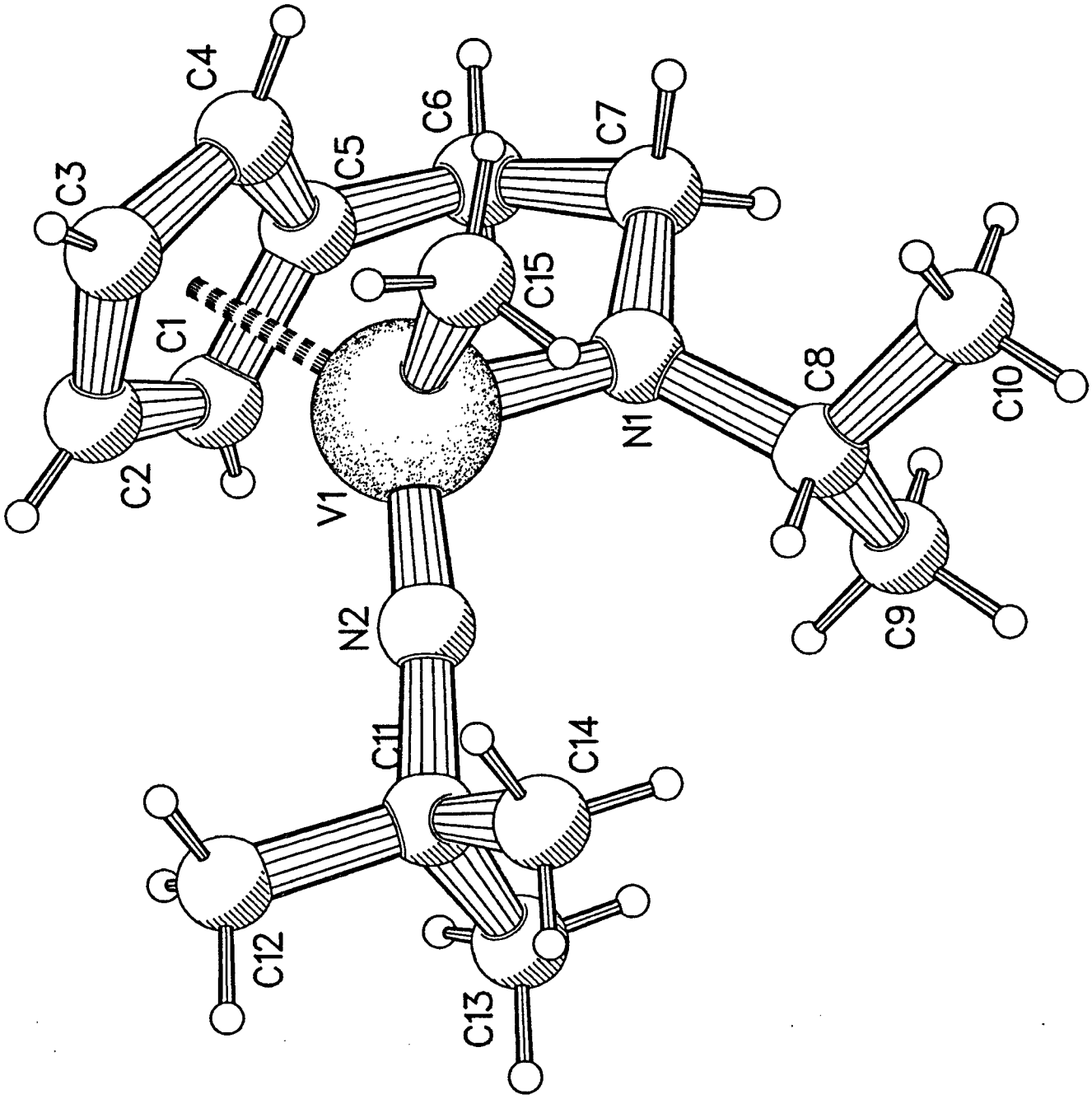
Torsion angles (deg.)

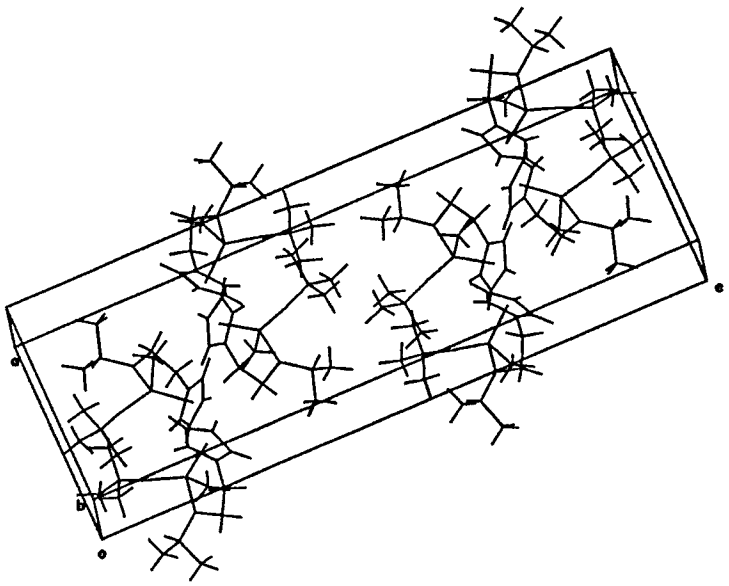
N(2)	-V(1)	-N(1)	-C(7)	165.2(2)
N(2)	-V(1)	-N(1)	-C(8)	-22.6(2)
C(1)	-V(1)	-N(1)	-C(7)	50.9(2)
C(1)	-V(1)	-N(1)	-C(8)	-136.9(2)
C(2)	-V(1)	-N(1)	-C(7)	43.3(3)
C(2)	-V(1)	-N(1)	-C(8)	-144.5(2)
C(3)	-V(1)	-N(1)	-C(7)	-5.4(3)
C(3)	-V(1)	-N(1)	-C(8)	166.8(2)
C(4)	-V(1)	-N(1)	-C(7)	-8.4(2)
C(4)	-V(1)	-N(1)	-C(8)	163.8(2)
C(5)	-V(1)	-N(1)	-C(7)	21.4(2)
C(5)	-V(1)	-N(1)	-C(8)	-166.4(2)
C(15)	-V(1)	-N(1)	-C(7)	-95.9(2)
C(15)	-V(1)	-N(1)	-C(8)	76.3(2)
N(1)	-V(1)	-C(1)	-C(2)	-170.82(18)
N(1)	-V(1)	-C(1)	-C(5)	-55.44(19)
N(2)	-V(1)	-C(1)	-C(2)	78.4(2)
N(2)	-V(1)	-C(1)	-C(5)	-166.25(18)
C(2)	-V(1)	-C(1)	-C(5)	115.4(3)
C(3)	-V(1)	-C(1)	-C(2)	-36.88(18)
C(3)	-V(1)	-C(1)	-C(5)	78.5(2)
C(4)	-V(1)	-C(1)	-C(2)	-77.9(2)
C(4)	-V(1)	-C(1)	-C(5)	37.45(18)
C(5)	-V(1)	-C(1)	-C(2)	-115.4(3)
C(15)	-V(1)	-C(1)	-C(2)	-56.9(3)
C(15)	-V(1)	-C(1)	-C(5)	58.4(3)
N(1)	-V(1)	-C(2)	-C(1)	12.8(2)
N(1)	-V(1)	-C(2)	-C(3)	-103.3(2)
N(2)	-V(1)	-C(2)	-C(1)	-111.18(19)
N(2)	-V(1)	-C(2)	-C(3)	132.7(2)
C(1)	-V(1)	-C(2)	-C(3)	-116.1(3)
C(3)	-V(1)	-C(2)	-C(1)	116.1(3)
C(4)	-V(1)	-C(2)	-C(1)	79.1(2)
C(4)	-V(1)	-C(2)	-C(3)	-37.04(19)
C(5)	-V(1)	-C(2)	-C(1)	38.00(18)
C(5)	-V(1)	-C(2)	-C(3)	-78.1(2)
C(15)	-V(1)	-C(2)	-C(1)	145.76(19)
C(15)	-V(1)	-C(2)	-C(3)	29.6(2)
N(1)	-V(1)	-C(3)	-C(2)	111.2(2)
N(1)	-V(1)	-C(3)	-C(4)	-5.2(2)
N(2)	-V(1)	-C(3)	-C(2)	-58.1(2)
N(2)	-V(1)	-C(3)	-C(4)	-174.59(18)
C(1)	-V(1)	-C(3)	-C(2)	37.92(19)
C(1)	-V(1)	-C(3)	-C(4)	-78.5(2)
C(2)	-V(1)	-C(3)	-C(4)	-116.5(3)
C(4)	-V(1)	-C(3)	-C(2)	116.5(3)
C(5)	-V(1)	-C(3)	-C(2)	80.1(2)
C(5)	-V(1)	-C(3)	-C(4)	-36.31(18)
C(15)	-V(1)	-C(3)	-C(2)	-153.9(2)
C(15)	-V(1)	-C(3)	-C(4)	89.6(2)

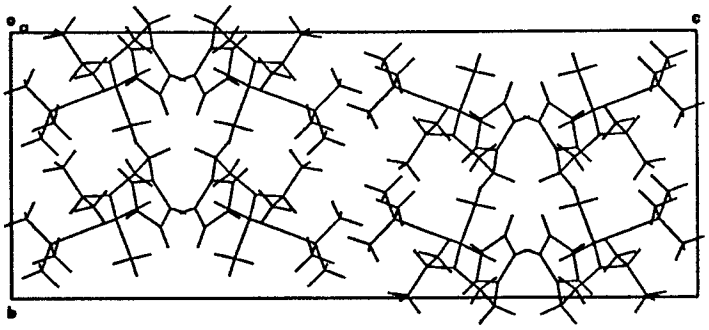
N(1)	-V(1)	-C(4)	-C(3)	176.09(19)
N(1)	-V(1)	-C(4)	-C(5)	58.14(18)
N(2)	-V(1)	-C(4)	-C(3)	11.4(4)
N(2)	-V(1)	-C(4)	-C(5)	-106.5(3)
C(1)	-V(1)	-C(4)	-C(3)	79.5(2)
C(1)	-V(1)	-C(4)	-C(5)	-38.47(17)
C(2)	-V(1)	-C(4)	-C(3)	37.08(19)
C(2)	-V(1)	-C(4)	-C(5)	-80.87(19)
C(3)	-V(1)	-C(4)	-C(5)	-118.0(3)
C(5)	-V(1)	-C(4)	-C(3)	118.0(3)
C(15)	-V(1)	-C(4)	-C(3)	-88.2(2)
C(15)	-V(1)	-C(4)	-C(5)	153.87(18)
N(1)	-V(1)	-C(5)	-C(1)	124.1(2)
N(1)	-V(1)	-C(5)	-C(4)	-120.80(18)
N(1)	-V(1)	-C(5)	-C(6)	3.4(2)
N(2)	-V(1)	-C(5)	-C(1)	22.6(3)
N(2)	-V(1)	-C(5)	-C(4)	137.8(2)
N(2)	-V(1)	-C(5)	-C(6)	-98.1(3)
C(1)	-V(1)	-C(5)	-C(4)	115.1(3)
C(1)	-V(1)	-C(5)	-C(6)	-120.7(3)
C(2)	-V(1)	-C(5)	-C(1)	-37.97(19)
C(2)	-V(1)	-C(5)	-C(4)	77.16(19)
C(2)	-V(1)	-C(5)	-C(6)	-158.7(3)
C(3)	-V(1)	-C(5)	-C(1)	-78.9(2)
C(3)	-V(1)	-C(5)	-C(4)	36.22(17)
C(3)	-V(1)	-C(5)	-C(6)	160.4(3)
C(4)	-V(1)	-C(5)	-C(1)	-115.1(3)
C(4)	-V(1)	-C(5)	-C(6)	124.2(3)
C(15)	-V(1)	-C(5)	-C(1)	-144.95(19)
C(15)	-V(1)	-C(5)	-C(4)	-29.8(2)
C(15)	-V(1)	-C(5)	-C(6)	94.3(2)
V(1)	-N(1)	-C(7)	-C(6)	-42.3(3)
C(8)	-N(1)	-C(7)	-C(6)	144.7(3)
V(1)	-N(1)	-C(8)	-C(9)	118.2(3)
V(1)	-N(1)	-C(8)	-C(10)	-116.1(3)
C(7)	-N(1)	-C(8)	-C(9)	-69.2(3)
C(7)	-N(1)	-C(8)	-C(10)	56.5(4)
V(1)	-C(1)	-C(2)	-C(3)	65.4(2)
C(5)	-C(1)	-C(2)	-V(1)	-66.3(2)
C(5)	-C(1)	-C(2)	-C(3)	-0.9(4)
V(1)	-C(1)	-C(5)	-C(4)	-65.5(2)
V(1)	-C(1)	-C(5)	-C(6)	98.2(3)
C(2)	-C(1)	-C(5)	-V(1)	66.0(2)
C(2)	-C(1)	-C(5)	-C(4)	0.4(4)
C(2)	-C(1)	-C(5)	-C(6)	164.1(3)
V(1)	-C(2)	-C(3)	-C(4)	64.0(2)
C(1)	-C(2)	-C(3)	-V(1)	-63.0(2)
C(1)	-C(2)	-C(3)	-C(4)	1.1(4)
V(1)	-C(3)	-C(4)	-C(5)	61.8(2)
C(2)	-C(3)	-C(4)	-V(1)	-62.6(2)
C(2)	-C(3)	-C(4)	-C(5)	-0.8(4)
V(1)	-C(4)	-C(5)	-C(1)	62.8(2)
V(1)	-C(4)	-C(5)	-C(6)	-100.3(3)

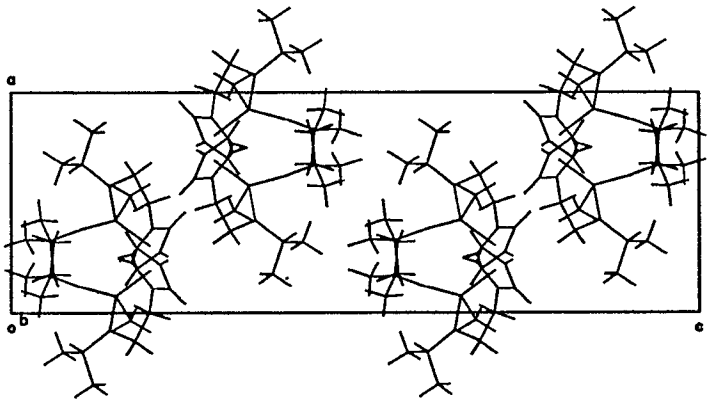
C(3)	-C(4)	-C(5)	-V(1)	-62.6(2)
C(3)	-C(4)	-C(5)	-C(1)	0.2(4)
C(3)	-C(4)	-C(5)	-C(6)	-162.9(3)
V(1)	-C(5)	-C(6)	-C(7)	-24.7(3)
C(1)	-C(5)	-C(6)	-C(7)	-102.1(4)
C(4)	-C(5)	-C(6)	-C(7)	58.3(5)
C(5)	-C(6)	-C(7)	-N(1)	40.7(4)

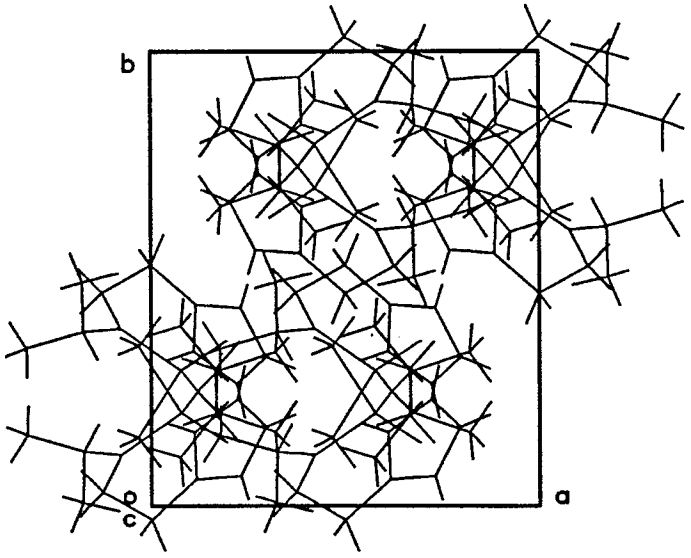
The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

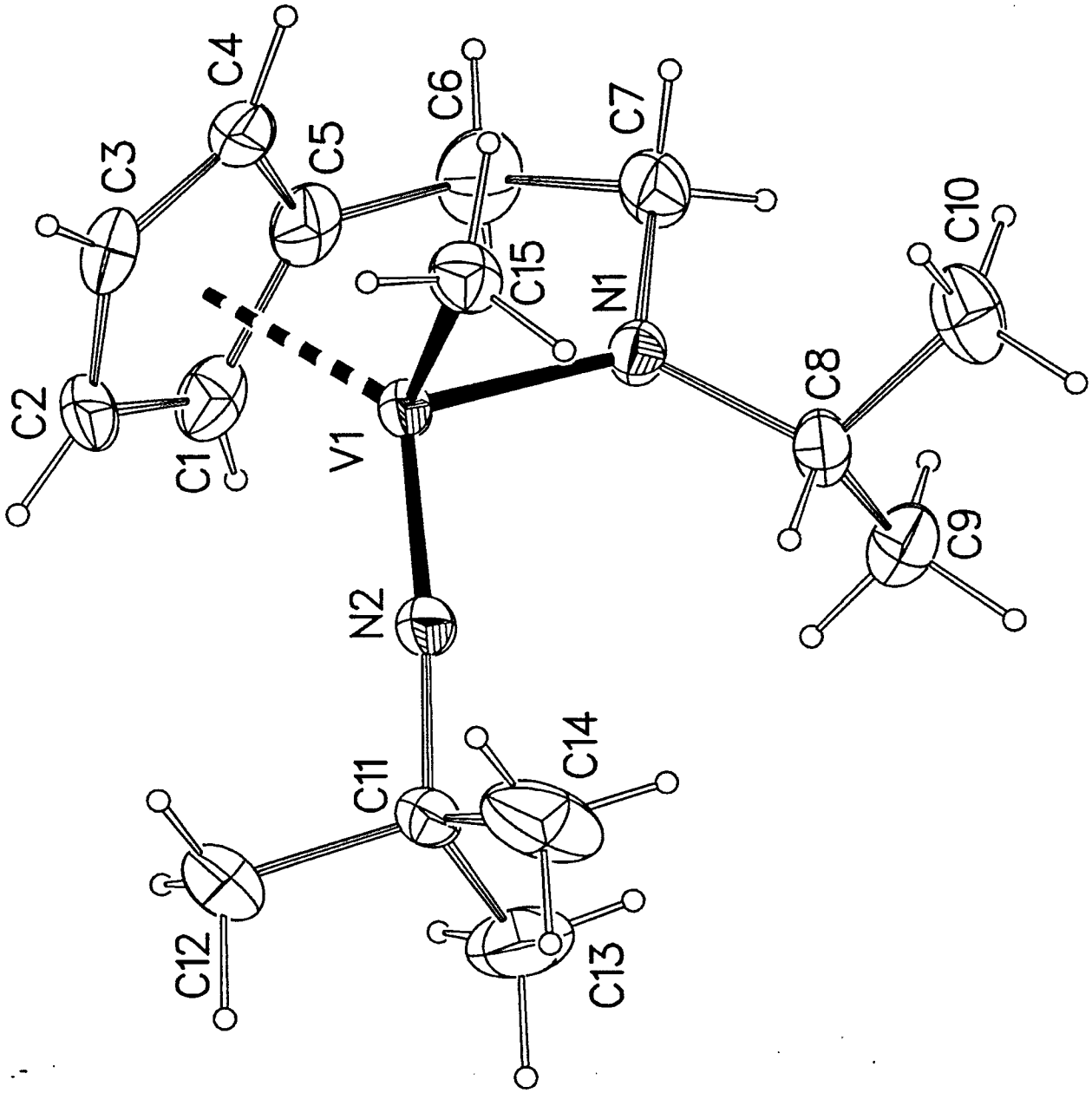

C4
C3
C5
C6
C7
C1
C15
C2
V1
N1
C8
C10
N2
C9
C11
C14
C12
C13








b
a
c


C4
C6
C7
C3
C5
C10
C15
N1
C2
C8
C1
V1
C9
N2
C11
C14
C12
C13